

REMARKS/ARGUMENTS**The Invention:**

Applicants' invention is a method for imparting a permanently roughened surface to a polyethylene object. Coatings do not readily adhere to polyethylene, which is the most resistant to coatings of all the polyolefins. Applicants have achieved permanent modification of the surface of even polyethylene by a method in which a coating of polyethylene powder admixed with inorganic particles is fused into the surface of a polyethylene object.

The claims of this application are limited to the treatment of polyethylene surfaces under heating conditions which melt the coating of polyethylene powders and the coated surface of the polyethylene object and fuse the coating into the surface of the object. Fusion of the coating into the surface of the polyethylene object can only be achieved by melting both the coating and the surface of the polyethylene object.. The significance of these limitations in distinguishing over the prior art is discussed in the following remarks..

The following publications are cited and relied on in the following arguments:

1. *Blow Molding Design Guide*, pages 182-184
2. *Heat of Fusion/Crystallization/Melting Point/Glass Transition by DSC* by Plastics Technology Laboratories, Inc, pages 1 and 2
3. *Plastics and Composites Welding Handbook*, edited by Grewell, Benatar and Park, pages 23-25
4. *Plastic Films*, by Osborn and Jenkins, pages 13-15

Copies of the cited publications are included in the Appendix.

Applicants' Arguments:

The teachings of the Jenett 2628172 patent are clear and unambiguous. The Jenett coating which is applied to the surface of a plastic object is to be heated to a temperature that is 80° C. to 5° C. below the melting point of the base (coated surface); claim 3, lines 32-36. Jenett states that the heating should raise the coating to an elevated temperature below the softening point of the base to fuse and level the polyethylene coating and form a homogeneous film (col. 2, lines 24-28). Jenett restates this at col. 4, lines 63-64, as: heating at an elevated temperaturebelow the softening point of the base..." See also col. 5, lines 39-40 where it is stated: "up to just below the melting point of the base"

Thus, two limiting properties of the base polymer are prescribed by Jenett.

These are the melting point and the softening point. Whether Jenett intended to equate the softening and melting points of the base polymer is not material. What is material is that Jenett never refers to a melting point temperature. Instead, he refers to the actual condition of softening or melting of the base. Accordingly, any consideration that softening or melting of the base can occur below the “melting point temperature” or that the identification of a melting point temperature for a polymer can be ambiguous is not material in interpretation of this reference. If some portion of the polymer melts at a temperature below the “accepted” melting point temperature for the polymer, Jenett teaches that the heating must be 5° to 80°C. below that temperature.

What is convincing clear from Jenett’s teachings is that he does not wish to cause any melting of the base polymer. Without melting of the base polymer there can be no fusion of the coating and the base, as will be pointed out later with reference to the *Plastics and Composites Welding Handbook* publication. One skilled in the art would have to proceed in contradiction to Jenett’s teachings to arrive at applicants’ invention, and this would not be obvious.

Even, however, if these arguments are not considered persuasive, the examiner’s position that polymers melt over a wide temperature range which occurs below an “accepted” melting point temperature is incorrect as applied to polyethylene.

Polyethylene is a crystalline polymer and as a crystalline polymer, has a narrow melting range. This is exemplified by the differential thermal analysis (DTA) graph of a crystalline polymer that appears in *Plastic Films*, page 14, which is reprinted below, where T_g is the glass transition temperature and T_m is the melting point temperature of the polymer:

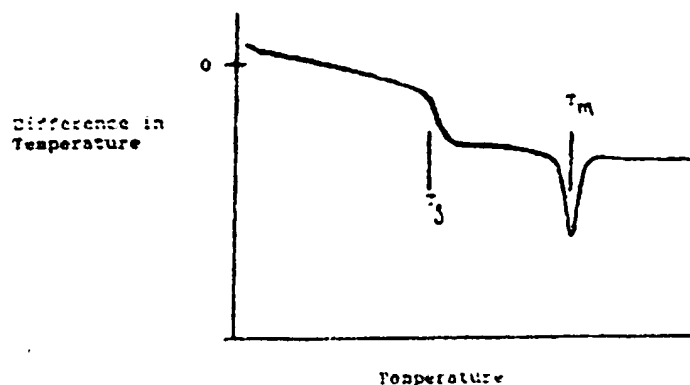


Figure 1.11 Schematic DTA Curve Showing Thermal Transitions

The cited publications evidence that polyethylene is a crystalline polymer with a narrow-range melting temperature.

“At a high enough temperature, however, the forces binding the segments together in the crystal matrix are overcome and the crystal melts. This is a very sharp transition as shown in Figure 1.11 (T_m)” *Plastic Films*, page 14 (underlining added)

“Crystalline polymers are usually tougher, softer, and have high shrink rates when cooled. The melt ranges of these types of materials are usually narrow. Examples of crystalline resins are polyethylene and nylon.” *Blow Molding Design Guide*, page 184 (Underlining added)

“The melting point of a crystalline polymer is the temperature at which a crystalline polymer melts, while the glass transition temperature is the temperature at which an amorphous polymer or the amorphous part of a crystalline polymer goes from a hard, brittle state to a soft, rubbery state.” *Heat of Fusion/Crystallization/Melting-Point/Glass Transition by DSC* by Plastics Technology Laboratories, Inc., page 1

Melting of a crystalline polymer does not occur until the narrow melt range of the crystalline structure is reached. Fusion between crystalline or semi-crystalline polymers does not occur until the mated polymers are heated to the melt temperature of the crystalline polymer.

“Therefore, for semi-crystalline polymers at temperatures above T_m , intermolecular diffusion [fusion] is very rapid and it is difficult to measure. Below T_m no welding or intermolecular diffusion takes place due to the crystals which bind the molecules.” *Plastics and Composites Welding Handbook*, edited by Grewell, Benatar and Park, page 25

Applicants' Claims:

The claims of this application recite that both the coating and the coated surface are heated to the melt temperature of the polyethylene part, which for

polyethylene (a crystalline or semi-crystalline polymer) is the narrow-range melt temperature of the crystalline phase; see the citation from *Heat of Fusion/Crystallization/Melting Point/Glass Transition by DSC*.

The claims further recite that the heating is sufficient to fuse the coating into the surface, a result which cannot occur without melting of the crystalline phase, by heating to or above the narrow melt range of the surface of crystalline polyethylene; see the citation from *Plastics and Composites Welding Handbook*.

Rebuttal to the Examiner's Arguments:

The examiner has cited page 307 of *Polymer Science Dictionary* to support the rejection by the assertion that the melting of a polymer is not instantaneous but instead occurs over a wide range of temperatures. While this assertion may be correct for amorphous polymers, it is erroneous when applied to polyethylene which is crystalline or semi-crystalline; see *Blow Molding Design Guide*, page 184 and *Plastic Films*, page 14. More importantly this assertion begs the issue. Jenett does not refer to the melting temperature of the polymer base. Jenett refers to the melting point of the polymer base. If some melting occurs at a temperature below the "accepted" melting temperature of the polymer base (as the examiner asserts), then a melting point is achieved, and Jenett teaches that the heating must be below that temperature.

This is a distinction which can not be minimized by asserting that there is an insignificant difference in the maximum temperature of heating in Jenett and the minimum heating temperature recited by applicants' claims. This is in reference to the following statement of the examiner in the final rejection:

"Thus the sole difference between the claims and combination of references is that Jenett just approaches the melting point whereas Applicants just reach the melting point, so the difference is a matter of one or a few degrees."

The entire heat of fusion of the polyethylene polymer is transferred at its narrow-range melting point. Note the sharp increase in the temperature difference between the reference and the sample shown in the DTA curve when the melting point of the crystal structure of the polymer is reached. This evidences the phase change of a crystalline polymer from a solid to a liquid occurs with a very slight change in temperature. This occurs in applicants' invention and is the precise condition which Jenett teaches must be avoided. This is not a minimal, insignificant, trivial or unobvious difference.

The examiner then states that in this instance, it is incumbent upon Applicant to establish criticality of this difference. Applicants submit that they have already established the criticality of the difference. Without melting of the base surface, the coating can not fuse into the base surface; and without fusion of the coating into the base surface, there can be no permanency of the coating.

The examiner has also suggested that since Jenett states that his coating is bonded “permanently” to the film base, he must have achieved melting of the base. That suggestion is erroneous for it contradicts the express intent of Jenett, i.e., that the maximum temperature of heating must be below the melting point of the base or substrate. The statement, which appears at column 5, lines 50-54 of the patent actually epitomizes the distinction between Jenett’s and applicants’ inventions. Jenett states that his coating is fused into a continuous film which is bonded to the base or substrate. “Bonding” is adhesion, not fusion; see *Plastics and Composites Welding Handbook.*, page 23 where the following is stated:

“Unlike adhesion, which relies on surface energetics (or secondary chemical bonds between dissimilar materials), autohesion relies on chain entanglement and secondary bonds for polymer chains of similar materials. Under ideal conditions, the diffusion is complete when the interface is no longer discernible from the bulk.”

[Underlining added]

Again the examiner’s suggestion begs the issue, for the rejections are made on the basis of obviousness under 35 U.S.C. §103, not anticipation under 35 U.S.C. §102. The only issues are what does the reference teach and whether or not the differences between that teaching and the claimed invention would have been obvious to one of ordinary skill in the art That requires no speculation: Jenett clearly and unambiguously teaches that the heating must stop 5° to 80°C. below the melting point of the polymer, i.e., before any melting of the polymer occurs. How could it be obvious to one of ordinary skill to ignore such an explicit teaching of the prior art?

The Hoopman et al reference has been cited for a suggestion of incorporating inorganic particles in the coating composition of Jenett. Hoopman et al disclose coating a backing with a mixture of inorganic particles in a binder, i.e., glue. The examiner has argued that the drawings illustrate that the solids are dispersed in the binder (glue) phase and are thus fused into the base sheet. This confuses the difference between surface adhesion and fusion. The inorganic solids are dispersed into the binder phase and the binder phase is adhesively bonded to the base sheet; note the line denoting the interface between the front surface 11 of the backing and

the abrasive composites 15 in Fig. 10, and the line denoting the interface between the continuous land layer 27 of the abrasive composite material and the backing 26 in Fig. 2 of the patent. There is no fusion of the coating into the base..

The Brant et al reference discloses coating a tackifier onto a film of a copolymer of ethylene and a C₃ to C₁₂ olefin comonomer to obtain a cling film. There is no suggestion that a tackifier which functions in the prior art to impart a cling property to a dry film would be functional as a tackifier for a liquid coating, nor is there any suggestion in Jenett that such a tackifier would be of any benefit in the Jenett coating.

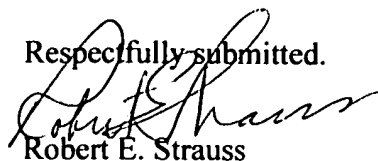
The Kagota et al patent has been cited for a suggestion of suspending polyethylene and a tackifier in water for use as an adhesive. This patent, however, teaches that it is necessary to incorporate hydrophilic groups, i.e., carboxyl groups, in the polyethylene; see column 3, lines 32-52. Again, as with Hoopman et al and Brandt et al, there is no teaching which cures the defect in Jenett, i.e., the failure to disclose heating of a coated surface to the melt temperature of the coated article to achieve fusion of the coating into the surface.

Summary of Applicants' Arguments:

In summary, the prior art is the antithesis of obviousness of Applicants' claimed invention. The prior art (Jenett) explicitly teaches one not to heat the coated polymer surface to its melting point. Applicants require that the polyethylene coating and the polyethylene base must be heated to the polyethylene melt temperature so that the coating fuses into the coated surface of the polyethylene object. This difference between the prior art and applicants' claims cannot be blurred by asserting that polymers generally do not have sharp melting points, nor trivialized by asserting that in any event, this is nothing but a few degrees differences in temperatures. Water turns to ice, and ice turns to water at 0°C, depending on the direction of the heat transfer. Is this also insignificant because it occurs at the same temperature?

The claims are believed to be of proper form and scope and recite invention over the prior art. Examination and allowance are solicited.

Respectfully submitted.



Robert E. Strauss

APPENDIX

The following publications are included herein:

1. *Molding Design Guide*, pages 182-1844
2. *Heat of Fusion/Crystallization/Melting Point/Glass Transition by DSC* by Plastics Technology Laboratories, Inc., pages 1 and 2
3. *Plastics and Composites Welding Handbook*, edited by Grewell, Benatar and Park, pages 23-25

Plastics and Composites Welding Handbook

Edited by

David A. Grewell, Avraham Benatar, Joon B. Park

With contributions by

C. Bonten, C. Brown, F. Chipperfield, J. P. Dixon, I. Froment, T. Hutton,
E. Pecha, P. Rooney, A. Savitski, C. Tüchert, R. Wise, C.-Y. Wu

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Hanser Publishers, Munich

Hanser Gardener Publications, Inc., Cincinnati

2.5 Intermolecular Diffusion

Once polymer-to-polymer contact is achieved at the interface, intermolecular diffusion and entanglement is needed to complete the process and to form a good weld. Autohesion is the phenomenon describing the intermolecular diffusion and chain entanglement across a thermoplastic polymer interface forming a strong bond (see Fig. 2.14). Unlike adhesion, which relies on surface energetics (or secondary chemical bonds between (dis)similar materials), autohesion relies on chain entanglement and secondary bonds for polymer chains of similar materials. Under ideal conditions, the diffusion is complete when the interface is no longer discernible from the bulk.

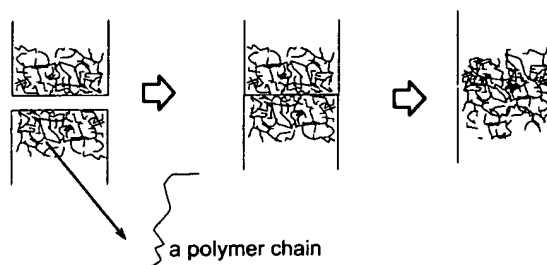


Figure 2.14 Intermolecular diffusion across an interface

The autohesion process is often divided into five phases:

1. Surface rearrangement
2. Surface approach
3. Wetting
4. Diffusion, and
5. Randomization

In welding, surface rearrangement, approach and wetting can be regarded as part of the pressure step. Diffusion and randomization are part of the intermolecular diffusion step.

The motions of individual linear polymer chains are modeled using the reptation theory developed by DeGennes [11, 12]. In the reptation model, a chain is confined into an imaginary tube that represents the constraints imposed by adjacent chains. The chain is free to move in a snake like motion within the tube, but it cannot leave the tube except at the ends (see Fig. 2.15). Over a period of time, the chain can slip out of its original tube. The motion of the ends of the chains, out of the original tube, propagates toward the center of mass of the chain until the whole chain is out of the original tube and a new tube is generated. In reality, many new tubes are generated during the elapsed time period, but all of these are partially made up of the original tube (see Fig. 2.15). Therefore, there are

two time scales in the reptation model: T_e is the time associated with short-range motions or wriggling of a chain within its tube, and T_r is the time required for the chain to generate a new tube. Since, for autohesion, motion outside the tube is necessary but generation of a new tube is not required, the time scale of importance for autohesion is in the range of $T_e < t < T_r$ [13]. Also, T_e is proportional to the molecular weight squared, and T_r is proportional to the molecular weight cubed [11]. Because the molecular weight is usually very large, $T_e \ll T_r$, and, for all practical purposes $t > T_e$ for $t > 0$. Therefore, during the time range $0 < t < T_r$, it is possible to relate the mean square path ($\langle \ell \rangle$) of the diffused chain length (ℓ) to the average interpenetration distance (X) of the chains across an interface (or even an imaginary plane in the bulk) [13].

$$X^2 \propto \langle \ell \rangle \quad (2.9)$$

During the early stages of diffusion and randomization ($t < T_r$), Kim and Wool [13] show that ℓ is proportional to $t^{\frac{1}{2}}$. Therefore,

$$X \propto t^{\frac{1}{4}} \quad (2.10)$$

Wool and O'Connor [14] proceed further to relate the interpenetration distance to the stress at fracture and time. The stress at fracture is proportional to the average interpenetration distance, therefore

$$\sigma_f \propto t^{\frac{1}{4}} \quad (2.11)$$

where σ_f is the fracture stress. They also derive relations for the time for complete healing (complete intermolecular diffusion), with respect to the molecular weight, temperature, and pressure.

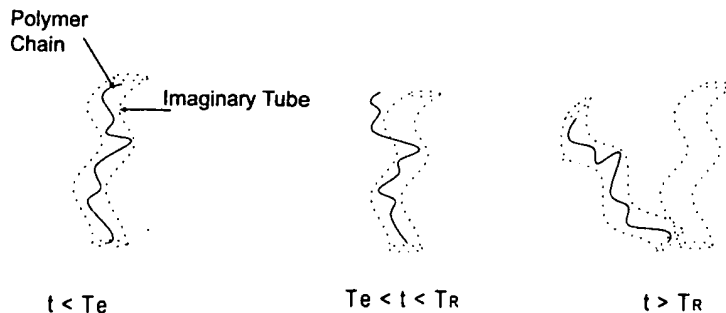


Figure 2.15 Imaginary tubes are used to describe the constraints applied onto diffusion polymer chains by adjacent chains

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Figure 2.16

Many investigators [6, 13–15] have found agreement between experiments and the relations presented above. The experiments and the theoretical work presented so far have been primarily for amorphous thermoplastics. For amorphous polymers, intermolecular diffusion can take place at any temperature at or above T_g . This theory can also be applied to semi-crystalline polymers, provided that the crystals are fully melted and the polymer chains behave as random chains; this is only possible at temperatures above the melting temperature (T_m), which is usually much higher than T_g . Therefore, for semi-crystalline polymers at temperatures above T_m , intermolecular diffusion is very rapid and it is difficult to measure. Below T_m no welding or intermolecular diffusion takes place due to the crystals which bind the molecules. Therefore, in order to estimate the diffusion time for semi-crystalline polymers, the results from experiments with amorphous polymers need to be applied.

2.6 Cooling

The final step in the welding process is the cooling and re-solidification of the polymer at the joint. During this final step, semi-crystalline matrices re-crystallize to obtain their final micro-structure, while amorphous polymers retain any molecular orientation that was previously induced. In addition, thermally induced residual stresses and distortion remain frozen in the parts.

For amorphous polymers, the pressure step results in molecular orientation parallel to the weld line, which is frozen in during cooling. Figure 2.16 shows evidence of frozen-in molecular orientation in hot plate welded polystyrene by photo-elastic fringe lines near the weld interface. Triumalai and Lee [15] also showed that reheating and melting of the polymer near the weld line resulted in shrinkage transverse to the weld due to molecular orientation.

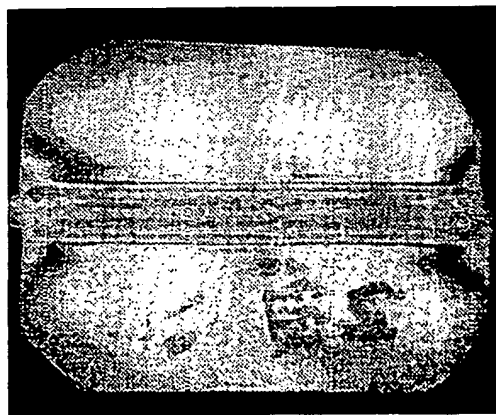


Figure 2.16 Photo-elastic fringe lines showing evidence of frozen-in molecular orientation [15]

Norman C. Lee

Blow Molding Design Guide



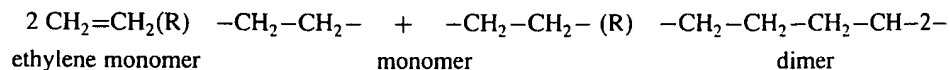
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carbon. It has several isotopic weights (i.e., 12, 13, and 14 or 6, 7, or 8 neutrons). This is the reason the atomic weight of carbon is 12.011, because it is a matched average of the 12, 13, and 14 mass types. Different elements can join together to form other substances with unique and different properties. For example, two atoms of hydrogen plus one atom of oxygen combine to produce a water molecule.

A molecule is a distinct substance formed by the joining of two or more elements. On a more macroscopic level, different atoms and molecules can combine to form compounds with defined atomic ratios. These may have the same formula but different weights owing to the isotopes found in elements. Once again using water as our example, if the hydrogen is the first isotope we get ordinary water. When it is the second or third isotope we get heavy water because of the deuterium or tritium forms of hydrogen.

All of the materials (polymers) used in blow molding today are compounds of basic elements and compounds processed and developed by the petrochemical industry. Basically, they are based on hydrogen and the class of material is generally referred to as hydrocarbons. Resin manufacturers develop special catalysts and processes to tailor make compounds that will suit the needs of their customers. By way of explanation, typical hydrocarbons such as polyethylene:



can join upon application of heat and in the presence of special catalysts. The process shown above converts two (2) molecules of ethylene into two (2) activated monomers that can join to form a dimer of ethylene. Continue this process thousands of times and a multiunit (polymer) chain of polyethylene will form. The catalyst controls the way in which the polymer grows and thus its final bulk properties. At high temperatures the chains of polyethylene are long coils. When melted, they are moving very rapidly. When cooled, they lose motion and become "glassy." They are clear at this point. Then something happens, in a way not unlike an old-fashioned carpenter rule, the chains start folding back on themselves and become crystalline. The previous clarity is lost and the material now becomes cloudy or opaque. While the material is cooled to ambient temperature, the state or morphology of the polyethylene becomes position, blow molding or injection molding, it occurs in the feed and compression sections of the screw pushing the polymer into the mold. As the polymer cools in the mold, the crystalline domains that existed in the pellets or flakes being molded reform as the molded part cools. The change in volume that occurs during recrystallization accounts for the mold shrinkage for these materials. Crystallization is influenced by the cooling time, melt temperature, and other factors. Variations in crystallinity in the part caused by these factors can introduce internal stress and warpage, often weakening the part.

12.2 Polymers

Polymers or resins (naturally produced products from trees and plants) are formed by a variety of chemical processes generally referred to as polymerization. This means that one

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or more types of less complex molecules are combined to form larger, much more complex molecules. Most importantly, these molecules or chains can be selectively produced to yield polymers or plastic materials of varying hardness, strength, color, weather resistance, or other properties to meet a wide range of applications. As previously noted, the monomer is the basic repeating unit in the polymer chain. It contains the elements of the final plastic. The normal form of a monomer is either a gas or liquid. It chemically unites under the right conditions with itself or other monomers to form the desired polymer.

12.2.1 Homopolymers, Copolymers, and Terpolymers

A polymer made up exclusively of a single monomer is called a homopolymer. Both polyethylene and polypropylene are often homopolymers. It was found that one can easily mix ethylene and propylene, the monomers for polyethylene and polypropylene respectively and get a completely different series of polymers. This type of polymer made up of two monomers is known as a copolymer. The properties are different from either homopolymer and thus become an important way to tailor make a desired polymer for an application. Another example to consider are monomers such as acrylonitrile, butadiene, and styrene. These three different monomers can be joined together to make three types of copolymer and two types of a more complex structure called a terpolymer. Examples of the latter are ABS plastic and nitrile rubber, both terpolymers in wide use today.

12.2.2 Thermoplastic and Thermoset Polymers

As previously noted, polymers may be classified into two major groups based on physical performance, thermoplastics and thermosets. Thermoplastic resins may be softened or melted and reshaped repeatedly by application of pressure and heat. This allows various forms and sources of reclaimed polymer from products to be reground and remolded many times. Thermoset materials, linked chemically during molding will degrade at a high temperature before molecular motion allows them to melt. This allows these materials to perform well in high temperature environments such as cooking appliance components and handles, automotive engine parts, electrical components for circuits and aerospace applications.

12.2.3 Amorphous and Crystalline

Thermoplastics can also be grouped into two structural categories, amorphous and crystalline. In an amorphous resin the molecules exist in a random state. These long chains are intertwined with each other, forming a glassy mass. In general, amorphous resins have less shrinkage when cooled. Processing amorphous plastics is generally easier because of a large melt temperature range which helps to minimize stress molded in a product. Products

made from these resins can be rigid with low to moderate impact strength (for example polystyrene or methol methacrate), or they can have excellent impact and clarity (as found in polycarbonate).

In a crystalline polymer, molecules orient in a more ordered fashion. The polymer chains essentially lie side by side in an orderly fashion. Crystalline polymers are usually tougher, softer, and have high shrink rates when cooled. The melt ranges of these types of materials are usually narrow. Examples of crystalline resins are polyethylene and nylon. Polypropylenes exhibit a range crystalline and amorphous behavior depending upon stereoisomer foam or a blend of them (Fig. 12.1).

12.2.4 Fundamental Properties

The physical performance of polymers can be summarized by characterization using a series of tests. An understanding will now be developed on how materials are classified (grade) by testing and how this information is used to pick an optimal material for a particular application. Throughout this section the designer needs to ask the following three questions:

1. What are the characteristics or properties of this material?
2. What role will these characteristics play in how the parts are molded?
3. Will these characteristics make the material suitable for the application?

The designer should also keep in mind four fundamental material concepts that could be the source of problems. This will allow the performance difference or variance to be traced:

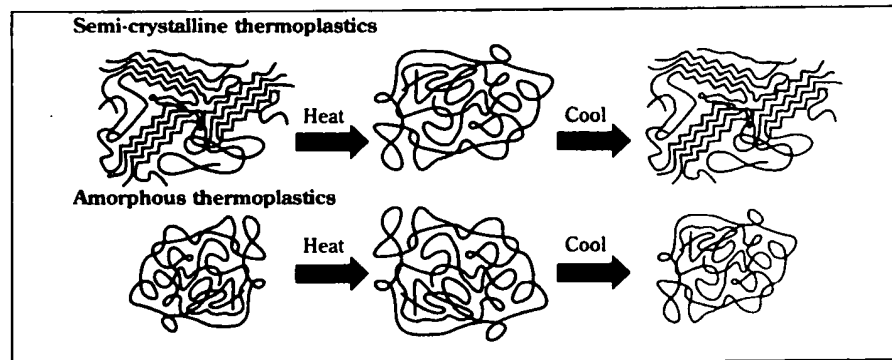
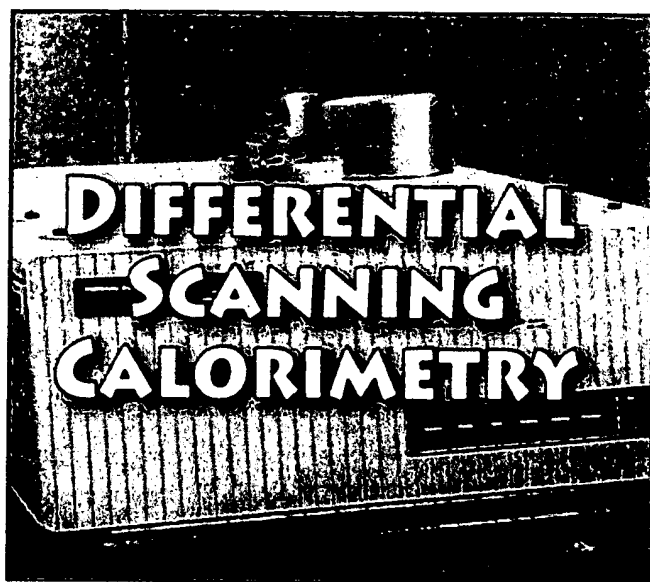


Figure 12.1 Most thermoplastics are either amorphous or semicrystalline. The crystalline regions of semicrystalline polymers, such as nylon or polypropylene, melt during plastication and reform during the cooling phase of the molding process. Amorphous polymers, such as polystyrene or acrylic do not exhibit this transition which means it does not crystallize, hence both materials have high clarity

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Heat of Fusion / Crystallization / Melting Point / Glass Transition by DSC (Differential Scanning Calorimeter)



ASTM
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E1356
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Scope:

Using a DSC (differential scanning calorimeter) the following are commonly found:

T_g = Glass Transition Temperature = The temperature (°C) at which an amorphous polymer or an amorphous part of a crystalline polymer goes from a hard, brittle state to a soft, rubbery state.

T_m = melting point = The temperature (°C) at which a crystalline polymer melts.

ΔH_m = the amount of energy in (joules/gram) a sample absorbs while melting.

T_c = crystallization point = is the temperature at which a polymer crystallizes upon heating.

ΔH_c = the amount of energy (joules/gram) a sample releases while crystallizing.

The data can be used to identify materials, differentiate homopolymers from copolymers or to characterize materials for their thermal performance.

Test Procedure:

A sample of 10 to 20 mg. in an aluminum sample pan is placed into the differential scanning calorimeter. The sample is heated at a controlled rate (usually 10°/min) and a plot of heat flow versus temperature is produced. The resulting thermogram is then analyzed.

Specimen size:

A sample weight of 10 to 20 mg is used.


 Differential Scanning Calorimeter (DSC)
Scan of Polyetheretherketone (PEEK)

Data:

A thermogram is produced which can provide Tg, Tm, ΔH_m or ΔH_c .

Equipment used at Plastics Technology Laboratories, Inc.:

Perkin Elmer DSC7 Differential Scanning Calorimeter

Mettler Balance

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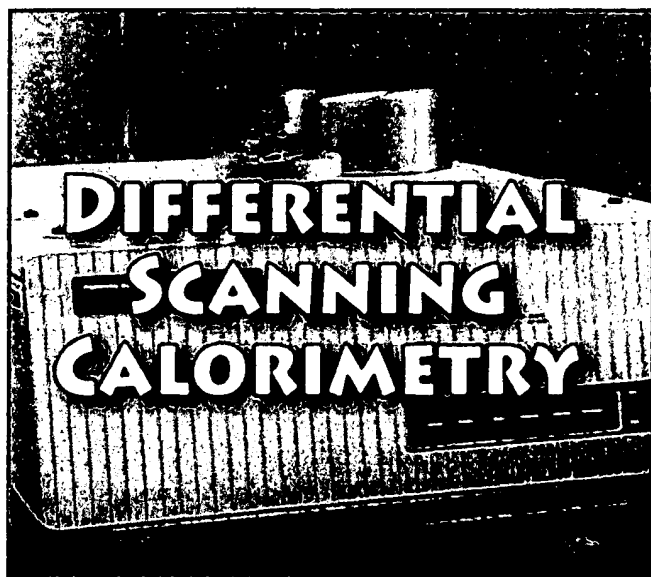
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Scope:

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T_g = Glass Transition Temperature = The temperature (°C) at which an amorphous polymer or an amorphous part of a crystalline polymer goes from a hard, brittle state to a soft, rubbery state.

T_m = melting point = The temperature (°C) at which a crystalline polymer melts.

Δ H_m = the amount of energy (joules/gram) a sample absorbs while melting.

T_c = crystallization point = is the temperature at which a polymer crystallizes upon heating.

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Specimen size:

A sample weight of 10 to 20 mg is used.

Differential Scanning Calorimeter (DSC)
Scan of Polyethersulfone (PES)

Data:

A thermogram is produced which can provide T_g , T_m , ΔH_m or ΔH_c .

Equipment used at Plastics Technology Laboratories, Inc.:

Perkin Elmer DSC7 Differential Scanning Calorimeter

Mettler Balance

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that is characteristic of the shear rate being applied. In extreme cases this can be seen as a decrease in the melt viscosity each time it is measured by quickly recovering and reprocessing the sample when it emerges from a capillary. This is an important factor in the design of the conditions for extrusion of polymers, as will be described in Chapter 2.

The properties of polymer melts stem from the principle that the stable state for a polymer molecule in a molten condition is a random coil highly entangled with its neighbors. For a solid polymer, however, the stable state is a more ordered one. Many polymers form crystalline domains similar in many respects to crystals formed from simple compounds like salt. The nature of these crystalline domains is highly sensitive to the structure of the polymer molecule.

CRYSTALLINITY IN POLYMERS

Crystalline and Amorphous Domains

As a polymer melt is allowed to slowly cool, the molecules tend to align themselves with their neighbors. Attractive forces between the molecules are re-enforced as the alignment becomes increasingly symmetrical. There is recent evidence that molecules also fold on themselves in parallel arrangement and that, in fact, this folding may be the dominant mechanism, with order increasing as neighboring molecules align themselves and fold on themselves. Whether by intermolecular alignment or intramolecular folding, as ordering approaches perfection and the melt begins to approach solidification, crystalline domains form. In these domains, the repeating units of the polymer chains occupy specific sites that form a symmetrical geometric solid. An example would be a tetrahedron with one unit in each corner. These crystalline domains grow to be quite large, often reaching the dimensions of a wave length of light, so that the resulting scattering of light causes haziness in films. Within a crystalline domain, units occupying neighboring sites can belong to different polymer chains. Thus, any given polymer molecule may wander in and out of several different crystalline domains. A large volume, containing many of these domains, consists of highly ordered and condensed crystalline areas with more open, disordered, or amorphous areas in between. These more disordered regions inevitably occur because as a polymer chain is being incorporated into a crystalline domain a point is reached where the next part of the molecule will not fit into the crystalline symmetry either because the molecule is so highly entangled with others or because some disruption such as a branch occurs. Thus, high molecular weight polymers are never completely crystalline and generally fall into the range of 20 to 90% crystallinity.

Response to Temperature

Crystalline domains increase in perfection by annealing. This implies that even in the solid state, polymer molecules or at least segments thereof have sufficient mobility at a certain temperature to be able to assimilate themselves better into a crystalline matrix. The initiation of this mobility occurs at the glass transition temperature (T_g) or the second order transition temperature. In a commonly used method, this temperature is determined by measuring the temperature difference between the polymer sample and an inert reference material as the temperature of the system is slowly raised at a constant rate. The polymer sample and the reference will heat up at the same rate, up to the point where segmental motion introduces a new mode of energy absorption. At this temperature an inflexion occurs in the plot of the temperature difference versus the temperature of the reference material, as shown schematically in Figure 1.11. This technique is called differential thermal analysis (DTA). In another technique, called differential scanning calorimetry, the energy required to maintain the temperature of the polymer sample and the reference material at an equal level is measured.

The segmental motion that begins at T_g occurs largely in the amorphous regions since in the crystalline regions, movement is restricted. As the temperature of the sample is increased further, segmental motion continually increases, primarily in the amorphous regions. At a high enough temperature, however, the forces binding the segments together in the crystal matrix are overcome and the crystal melts. This is a very sharp transition as shown in Figure 1.11 (T_m). The crystalline melting point and

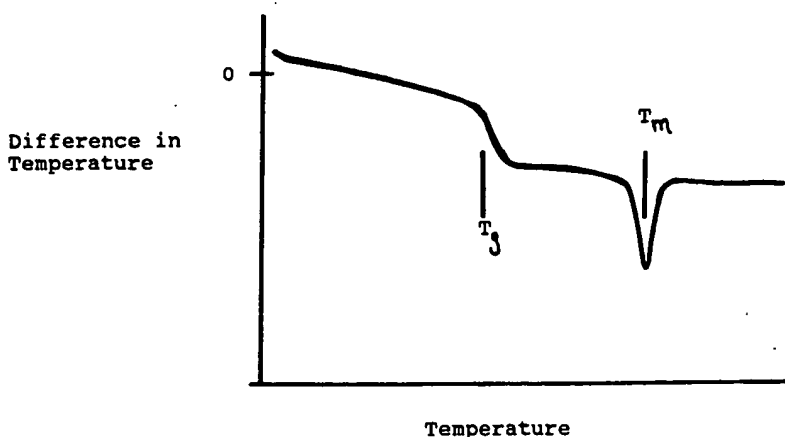


Figure 1.11 Schematic DTA Curve Showing Thermal Transitions.

the glass transition structure of

Measurements

As mentioned, the same procedure that they differ in photographic about the form of these versus

Another polymer amorphous region has a density of about 1.0 degree of crystallinity. One way to measure density seeking measurement gradient is essential mixtures of polymers, the noting the polymer

The Effect of

From the beginning of the molecule leads to the Since it exhibits polyethylene (tension and hence induced in the film both crystalline of polyethylene

Another way molecule is that which contain based on ethylene

Here, both the precisely controlled and is called LLDPE are typical

the glass transition temperature are dependent largely on the chemical structure of the polymer chain.

Measurement of Crystallinity

As mentioned above, crystalline domains of polymers exhibit some of the same properties as crystals of simple molecules. One characteristic is that they diffract X-rays, with the diffracted beam forming a pattern on a photographic plate. Analysis of this pattern leads to precise information about the form and dimensions of the crystal as well as the relative amount of these versus the amorphous areas.

Another property of crystalline regions is that they are denser than amorphous regions. For example, the most crystalline form of polyethylene has a density of about 0.96 whereas the least crystalline form has a density of about 0.88. Thus, for polymers of similar chemical structure, degree of crystallinity can be inferred from a knowledge of the density. One way to measure density is to immerse a sample in liquids of different density seeking one in which it neither sinks or floats. For many routine measurements of polymers within a limited range of densities, a density gradient is established in a large, glass cylinder by carefully filling it with mixtures of miscible liquids with the right range of densities. After calibration, the density of any polymer sample can be exactly measured by noting the position it assumes in the cylinder.

The Effect of Molecular Structure

From the description of crystalline and amorphous domains in the beginning of this section, it follows that the most linear polyethylene molecule leads to the highest degree of crystallinity (about 90%) in solid form. Since it exhibits the highest density (0.96) it is called high density polyethylene (HDPE). HDPE is not produced by free radical polymerization and hence has a very low degree of branching. For polyethylene produced in the free radical process, with its much higher level of branching, both crystallinity (50–70%) and density (0.91–0.92) are lower. This variety of polyethylene is called low density polyethylene (LDPE).

Another way to introduce disruptions in the linearity of a polyethylene molecule is to include a second monomer during the polymerization which contains a bulky side chain. An example would be a copolymer based on ethylene and a small amount of butene as shown in Figure 1.12.

Here, both the length and number of the side chains or branches are precisely controlled. This polymer is made by the same process as is HDPE and is called linear low density polyethylene (LLDPE). Densities for LLDPE are typically in the range of 0.94 to 0.95. With bulkier side chains,

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